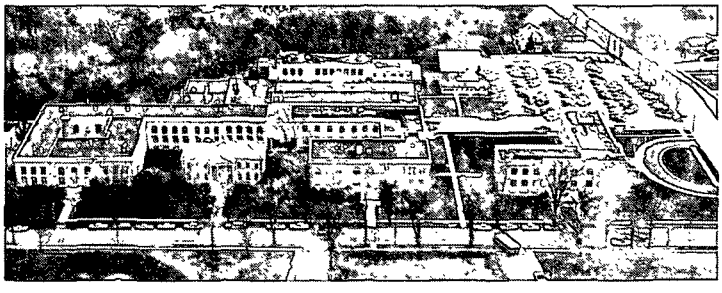

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CORROSION RATE MONITORING IN KRAFT PULPING PROCESS LIQUORS

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ABSTRACT

Corrosion monitoring in alkaline sulfide kraft pulping liquors has been performed by means of the linear polarization resistance and electrical resistance methods. Corrosion rates obtained in real and simulated white liquors are compared with weight loss results. The importance of Tafel constants to the linear polarization resistance measurements is discussed. The corrosion rates of four materials of construction are compared.

INTRODUCTION

The kraft process employs alkaline sulfide solutions to convert wood chips to wood pulp for use in making paper products. These solutions, called liquors, are regenerated in the process and pass through clarifiers before being charged into the process with the wood chips. Corrosion in clarifiers and associated tanks and piping decreases their useful life. This study is part of a larger effort to understand the corrosion process and identify ways to reduce the damage. Reliable monitoring techniques will aid in identifying periods during which corrosion rates are high.

Kraft white liquor is an aqueous solution of NaOH and Na_2S (pH 14.5) containing lesser amounts of Na_2CO_3, NaCl, $Na_2S_2O_3$, Na_2SO_4, Na_2SO_3, Na_2S_x (sodium polysulfide) and other minor constituents. The temperature during clarification and storage is usually 85-95 C.

Corrosion rates depend on the concentrations of corrosive species in the solution. As early as 1953, it was found that corrosion in white liquor was stimulated by increasing concentrations of Na_2S, NaOH, $Na_2S_2O_3$ and Na_2S_x.[1] Haegland and Roald[2,3] focused on the importance of the reduction of polysulfide in controlling corrosion rates. Polysulfides were also shown to decrease the critical current density to passivate the steel.[4] According to another study,[5] Na_2CO_3, NaCl and Na_2SO_4 slightly depressed the critical current; corrosion was increased if Na_2SO_3

concentration was less than 1 g/L. Singbeil and Tromans[6,7] observed that Na_2S increased the size of the active/passive peak. Corrosion potential was dependent on the Na_2S_x (polysulfide) concentration. This was confirmed later by Ahlers.[8] A laboratory study by Wensley and Charlton[9] revealed that the critical current for passivation was increased by NaOH, Na_2S and $Na_2S_2O_3$ but was not affected by Na_2SO_4, Na_2CO_3 and NaCl. In a field study of white liquor tanks[10] using weight loss coupons, they found that although carbon steels with high (Ni + Cr + Cu)/Si ratio experienced lower corrosion rates, liquor corrosivity had a stronger influence than steel composition. Other laboratory studies[11] of polarization behavior have demonstrated that behavior is affected by NaOH and Na_2S_x but not by Na_2CO_3, NaCl or $Na_2S_2O_3$. In long-term weight loss tests[12] additions of S (to form Na_2S_x or polysulfides) had a transient effect of increasing the corrosion rate. Additions of $Na_2S_2O_3$ increased the corrosion rate throughout an exposure by placing the corrosion potential at the active-passive potential. Minor changes in liquor composition were found to have a large influence on the corrosion rate.

Thus, corrosion rate may be affected by small changes in concentrations of oxidized sulfur species present due to process upsets, poor reduction of sulfur compounds in the recovery boiler or oxidation of the liquor by contact with the atmosphere. Monitoring the corrosion rate will aid in identifying liquor conditions which cause increased corrosion and will assist operators in correcting problems of which they are unaware, e.g., poor recovery boiler performance causing incomplete reduction of sulfur compounds.

Weight loss measurements have been most widely used to measure corrosion rates in white liquor[10] but there have been no published accounts of field applications of continuous monitoring of corrosion rates in white liquors. In an effort to qualify monitoring techniques for use in white liquors, Yeske[13] obtained results in the laboratory demonstrating the application of electrical resistance and linear polarization resistance to measurement of corrosion rates in white liquors. Electrical resistance results agreed closely with weight loss results. Empirical calibration of the LPR method was necessary for quantitative prediction of corrosion rates. Errors in LPR method were observed when carbon steel was at passive potentials where oxidation of sulfides in the liquor was possible.

The present study was aimed at obtaining corrosion data in white liquors on a continuous basis in operating equipment to identify the reasons for periods of high corrosion rate (presumably due to liquor changes) and was to demonstrate the use of various methods for corrosion monitoring. More specifically, the objective was to determine if the linear polarization resistance or electrical resistance methods could be used to obtain accurate, continuous measurements of corrosion rates of carbon steel in white liquor. The relative corrosion rates of four carbon steels also were determined.

EXPERIMENTAL PROCEDURE

This investigation comprised laboratory and field studies. Measurement methods were qualified in the lab before field testing. Weight loss coupons, linear polarization resistance (LPR) electrodes and electrical resistance (ER) probes were exposed simultaneously in simulated white liquors. Each weight loss and LPR electrode specimen was mounted on a threaded rod that penetrated the lid of the Teflon test cell. Sealing was provided by Hypalon gaskets. The weight loss coupons (and LPR electrodes) were cylindrical specimens of 1018 carbon steel 3/8-inch diameter with an exposed surface of 9 cm^2. Prior to testing, the coupons were polished to 120 grit, degreased and weighed. Solutions used in the laboratory studies were prepared in purged flasks using analytical reagents and distilled water purged with nitrogen. Solutions were changed in a glove bag under a nitrogen atmosphere to prevent oxidation by air. During

the tests, the solutions were maintained at 90 C. The heavy black deposits formed on these coupons during testing were removed before weighing by brief immersion in an inhibited Clarke's solution.[14] In some cases, mild abrasion was necessary to remove adherent deposits prior to acid cleaning.

All measured potentials have been quoted with respect to the silver/silver sulfide electrode, V(SSSE). These may be converted to the standard hydrogen scale, V(SHE) via the empirical equation:

$$V(SHE) = V(SSSE) - 0.7125 - 0.039 \log ([Na_2S]/858) \quad (1)$$

where $[Na_2S]$ is the sodium sulfide concentration in g/L, as described previously.[15]

Linear polarization resistance measurements were made using a 10 channel Petrolite M1010 corrosion rate instrument and occasionally via a PAR 350 Corrosion Instrument. The Petrolite instrument was programmed to impose alternate +10 mV and -10 mV polarizations of 15 minute duration on each of eight electrodes. Measurements of the open circuit potential of each electrode were made before each polarization. The current required to maintain the +/- 10 mV polarization at the end of the 15 minute cycle was converted by the instrument into an electrical signal proportional to the corrosion rate in mils per year (mpy) according to:

$$\text{Corrosion Rate (mpy)} = (1/2.3\ F)\ (\beta/z)\ (M.W./d)(\Delta i/\Delta E) \quad (2)$$

where F is Faraday's constant (96500 coul/mole of electrons), ΔE is the applied potential, Δi is the induced current, z is the number of electrons released in the dissolution reaction, MW is the molecular weight (g/mol) and d is density (g/cm^3). The instrument has a hard-wired value of β equal to 83.3 mV, where β is given by:

$$\beta = \beta a * \beta c / (\beta a + \beta c) \quad (3)$$

and β_a and β_c are the anodic and cathodic Tafel constants. The instrument also uses a value of z equal to 2. Equation (2) is based on the theory of Stern and Geary.[16] The name "linear polarization resistance" arises from the last term in Eq. (2), $(\Delta i/\Delta E)$ which has units of resistance. Others have reviewed the linear polarization resistance technique.[17,18]

During the laboratory study, the raw corrosion rate data and the rest potential data were stored on disc after processing by an Apple IIe microcomputer equipped with an ISAAC 91A Interface. Data were acquired, stored, plotted and printed automatically. The corrected measurements of corrosion rate were plotted vs. time. The average corrosion rate was determined. The corrosion rate data are presented as this average corrosion rate taken over the period of the exposure. In the field study, LPR results were recorded on charts and data were entered manually to computer file for subsequent use.

Electrical resistance measurements of the corrosion rate of carbon steel in simulated liquors were made using a Rohrback Corrosometer 4000 with wire element sensing probes of 1020 carbon steel (type W40 and W80). The Corrosometer provided a continuous digital indication of the normalized loss of wire cross section due to corrosion. This digital output was converted to an average corrosion rate by calculating the loss of wire thickness divided by the total exposure time according to the equation:

$$mpy = \frac{\Delta R\ (365)\ P}{\Delta t\ (1000)} \quad (4)$$

where ΔR is the change in dial reading and Δt is the exposure time in days. The factor P is a probe range multiplier factor. A dummy element in the probe is designed to correct for temperature fluctuations. Measurements were compared with weight loss of 1018 steel electrodes. During the in-mill testing, the electrical resistance (ER) tests were performed at Mills 3 and 4 only.

Weight loss coupons used in the field study were the same design as those used in the lab study and were prepared in the same way. The coupons were threaded onto glass-to-metal seals on a pipe section forming the end of a probe, with Hypalon gaskets between the samples and seals. The probe contained ten electrodes: eight for linear polarization resistance and weight loss testing, two silver/silver sulfide (SSSE) reference electrodes, and two additional weight loss specimens. Testing was performed on 1018, A285C, A283 and A285-SPEC steels of composition as listed in Table 1. During testing, the probe was suspended through a manhole in the roof of the tank or clarifier. After the test, the specimens were carefully blasted clean (glass beads) and weighed.

During mill testing, liquor was pumped from the tank and circulated through a valved sample bottle. When the corrosion rate exceeded a set point (75 mpy) on one of the 1018 electrodes used for LPR measurements, the valves operated and a sample of the liquor was retained in the sample bottle. Samples were returned to the Institute for acidimetric analysis of NaOH, Na_2S and Na_2CO_3, potentiometric titration of Na_2S_x and ion chromatographic analysis of Na_2SO_3 and Na_2SO_4 to determine whether the high corrosion rate was associated with any liquor constituents. Concentrations of dissolved metals were measured by emission spectrographic analysis.

The effect of liquor velocity was evaluated at Mill 4 by means of a simple weight loss test. Three weight loss coupons were exposed to the flowing liquor. Three more electrodes were exposed, but isolated inside a fine stainless steel mesh bag so that the liquor would enter, but flow would be minimized. Both protected and unprotected specimens were located on the same probe. This test of the effect of flow velocity was performed at the same location as the other weight loss, ER and LPR tests.

Polarization curves were obtained with a Petrolite Potentiodyne portable potentiostat. Scan rates of 0.1 mV/s were employed at mills 1 and 2 and a rate of 0.6 V/h (0.167 mV/s) was adopted at mill 4.

Mill 1 tests were performed in a white liquor tank where level fluctuated by as much as 16 feet. Tests at Mill 2, were performed in a clarifier which was always full and quiescent. Mill 3 tests were done in a white liquor day tank, under fairly turbulent conditions. Relatively quiet conditions were encountered at the last mill (4) in a clarifier.

RESULTS AND DISCUSSION

Linear Polarization Resistance Measurements

Laboratory Results. Preliminary testing of the LPR technique was conducted in the laboratory to determine if the method could be employed in white liquor, and to identify any sources of error. The corrosion rates measured by the LPR method were compared with rates measured using weight loss coupons. Although some variation of corrosion rates is anticipated with weight loss data, they were considered to give a true measure of the corrosion rate. Weight loss was determined for the same electrodes that were used in the LPR measurements.

Variations of linear polarization resistance measurements during the exposure of one electrode have been illustrated in Figure 1. Significant fluctuations in corrosion rate were observed. Changes in the liquor composition should not have occurred in the laboratory to cause fluctuations in corrosion rate. Fluctuations may have been related to wide variations in corrosion potential which have been observed during long-term weight loss tests in some solutions.[12] The corrosion rate may change significantly with changing corrosion potential. Steel in caustic solution has well defined active-passive behavior. A noteworthy result was obtained when thiosulfate was added. A transient increase in corrosion rate followed by a higher

steady-state corrosion rate was observed as illustrated in Figure 2. Initial fluctuation may have been related to changes in the corrosion potential. Temperature fluctuations also may have influenced the changes in measured potential. The periodic loss of some of the protective surface film or deposit from the electrode may cause fluctuations, also. The corrosion rate measured via the anodic polarization was higher than the rate measured via cathodic polarization.

The average corrosion rates of the laboratory tests are summarized in Table 2. The agreement between weight loss and average LPR corrosion rate is generally poor. The average corrosion rates measured by LPR were higher than the weight loss results, indicating that the LPR instrument overestimates the corrosion rate. The value of β/z = 41.65 mV hardwired into the instrument apparently is inaccurate for white liquors. Calculated values of β/z which would be required to obtain agreement between the weight loss measurement and the LPR measurement are denoted $(\beta/z)^*$ and are tabulated. They can be seen to be in the range 12-16 for the NaOH + Na_2S liquors. The values in thiosulfate solution were slightly higher (16.5-18.3), and in low concentrations of polysulfide were even higher (20.3 and 24). Very low values of $(\beta/z)^*$ (2.9-9.7) were required in solutions with high polysulfide concentrations.

Lower values of β/z would be expected if the true value of β is less than the value of β assumed by the instrument maker. Previous investigators have used different values. Singbeil and Tromans[19] assumed β_c to be 145 mV (a value published for hydrogen evolution[20]) and assumed β_a to be 72 mV for iron dissolution.[21] At this laboratory, in a number of liquors containing S additions,[12] the average β_a was 68 mV and the average β_c was 128 mV. In the present work, measurements of Tafel slope in the simulated white liquor were obtained from polarization curves as illustrated in Figure 3. The anodic Tafel region was short due to the adjacent active-passive transition, making an accurate measurement difficult. From these measurements, summarized in Table 3, average values of β_a = 35 and β_c = 118 mV were obtained. A value of β = 35 was calculated and assuming z = 2, β/z was calculated to be 17.5. This agreed well with the values required to bring weight loss and LPR measurements into agreement in Table 2. The β/z value used by the instrument is too large by a factor of approximately 2.3. Values from the Petrolite instrument could be corrected by dividing by 2.3 to make β/z = 18, as described by Yeske.[13] In lab tests, if the LPR measurement was adjusted so that β/z equaled 18 mV, accurate results were obtained when the steel was actively corroding and the open circuit potential was below -100 mV.

The β/z ratio required in different liquors may vary between tests due to differences in concentrations of species which change the corrosion potential. The values of β may vary depending on the corrosion potential of the steel, with different reactions predominating at different potentials. At passive potentials, where the electrode becomes film covered, Tafel behavior may degenerate. Formation of a passive film on the surface will impede dissolution.

Bandy and Jones[22] have investigated the errors due to nonlinearity for some combinations of β_a and β_c, i.e., the error arising because the polarization curve is not linear in the range -10 mV to +10 mV. They found that the error was as high as -50% for the anodic polarization and +30% for the cathodic polarization. In the present study, the errors due to nonlinearity were minimized by averaging the anodically and cathodically determined corrosion rates.

Variations of z may also change the β/z ratio. Iron sulfide, FeS, is the usual corrosion product in NaOH/Na_2S solutions. Formation of FeS by dissolution to Fe^{++} or $HFeO_2^-$ and subsequent precipitation of the sulfide generates 2 electrons per atom of Fe dissolved. In solutions containing a high concentration of $Na_2S_2O_3$, the corrosion

product was found to contain $NaFeS_2$ in addition to FeS. The iron in this compound presumably has an oxidation state III but it is not known what fraction of the product is $NaFeS_2$. For this reason, the value of z is uncertain. $NaFeS_2$ may be less protective[13] or soluble.[23] Using the measured Tafel slopes in simulated white liquor solutions containing $Na_2S_2O_3$, z = 2 was required to obtain agreement, so that $NaFeS_2$ formation does not seem to have an effect. However, the change of Tafel slopes on the surface due to corrosion deposits may be a compensating factor. Further work is required to determine the effect of $NaFeS_2$ formation.

In solutions with enough polysulfide to achieve spontaneous passivation, β/z values of 3-10 mV were required to obtain agreement between LPR and weight loss results. These values indicate that the measured LPR rates were much higher than the actual rates. The electrodes actually are passive and corroding at a low rate as determined by weight loss. The discrepancy between the actual corrosion rate on passivated steel and the rate determined by LPR methods is related principally to liquor oxidation effects. Large currents measured at these potentials are due to liquor oxidation, in which sulfide is oxidized to polysulfide and thiosulfate.[23] Currents due to these secondary reactions increase the measured values but the true corrosion current remains low. Liquor oxidation does not affect LPR values at lower potential; at -240 mV(SSSE), the current due to oxidation of sulfides has been calculated to be $<1\ \mu A/cm^2$,[13] which should have a negligible effect on corrosion rates measured at those potentials. Another source of differences is that βa and βc were determined at active potentials and are not relevant in the passive region where βa may be infinite.

Corrosion Monitoring in the Field. The field study of corrosion rates in white liquor tanks and clarifiers demonstrated considerable fluctuation of corrosion rate measured by LPR as illustrated in Figure 4. Similar behavior was observed for other electrodes but the 1018 showed the most variation. The surface film may be less protective or more easily damaged on 1018 electrodes. The corrosion potential was observed to fluctuate similarly and the changing corrosion rate may be related to this fluctuation. The cause of the fluctuations did not seem to be related to significant changes in liquor composition as shown in Table 4, although Figure 2 shows that small changes in liquor composition can accompany large transient increases in corrosion rate. It may be speculated that a slowly increasing concentration of some harmful species such as $Na_2S_2O_3$ could maintain the high transient currents for longer periods. Generally, E_{corr} became more noble and the corrosion rate declined with exposure, presumably due to the formation of a protective film. This result confirms the importance of E_{corr} in determining the corrosion rate. It also indicates that chemical species in the liquor which place the corrosion potential in the active-passive range will cause increased corrosion rates.

The corrosion rates determined by LPR and weight loss are summarized in Table 5. There was again poor agreement between the weight loss and the LPR measurements obtained directly from the instrument. Values of $(\beta/z)^*$ required to obtain agreement with the weight loss results average 25 mV. These values are considerably higher than values required in simulated white liquor (18 mV). The $(\beta/z)^*$ values required for the real liquor may be rationalized if Tafel slopes are considered. Tafel slopes were measured from polarization curves obtained in the test mills. Figure 5 illustrates a representative polarization curve obtained in a mill. The Tafel constants are listed in Table 6 and have average values of β_a = 70 mV and β_c = 125 mV, from which β is calculated to be 44.8 mV and β/z = 22.4. This value is reasonably close to the average value of $(\beta/z)^*$ required (25 mV) in Table 5.

The different $(\beta/z)^*$ values for the field study resulted from different

Tafel slopes. Species not present in simulated white liquors may give rise to these differences. The actual kraft white liquors contain a multitude of minor constituents. These constituents may exert a strong influence on the electrode kinetics, reflected in the change in Tafel slopes. Moreover, they may affect the corrosion potential and different reactions may predominate compared with the lab study. For example, polysulfide at intermediate concentration controls the corrosion potential in the active/passive range (and in the passive region when present in sufficient quantities). Thiosulfate impairs passivation and the corrosion potential remains in the active-passive range.[12] Other species may affect the corrosion potential and kinetics in ways that were not discovered in the study of simulated white liquors.

The LPR method possesses some important advantages in corrosion measuring. It responds instantaneously to changes in liquor corrosivity, and provides more information on the corrosion process. The method is suitable as a basis for automatic measurements in operating equipment. These advantages must be considered of sufficient value to justify the effort of measuring Tafel slopes and calibrating the LPR measurement with weight loss testing.

Electrical Resistance Measurements

Corrosion rates determined by ER for simulated white liquor in the laboratory test are illustrated in Figure 6. The corrosion rates obtained in the field tests, Figure 7, indicated that a test period of about 30 days is required to get a stable measurement of corrosion rate in agreement with weight loss results.

Electrical resistance measurements obtained in the laboratory and field agreed very well with corrosion rates obtained by weight loss tests, Table 7. The agreement between the actual corrosion rate and the ER measurement is acceptable in the three liquors producing corrosion rates from 5 to 40 mpy. It is worth noting that the ER method accurately monitored a low corrosion rate in the high polysulfide liquor, whereas uncertainties in interpretation were encountered with the LPR methods used in polysulfide liquors. Film formation on the electrode also had little effect, although unusual resistance changes were evident at the start of the three tests. The resistance actually decreased during the first 24 hours. While this anomaly may be attributed to the precipitation of a conductive deposit on the wire, it may also have been due to failure to achieve temperature equilibrium at the temperature compensating element at the time of the first resistance measurements.

The ER method has a number of advantages. It is useful where there is no information available on the Tafel slopes or the corrosion mechanism is not understood because the method does not require calibration or interpretation. Data are in a form which are easy for operating personnel to interpret. The ER method is also suitable for use in circumstances where the electrode is not continuously immersed, e.g., at liquid level lines. On the other hand, comparison of various materials would be awkward because electrodes would have to be manufactured of each material at greater expense than the cylindrical specimens used in the weight loss and LPR tests. Another drawback of this method is that it does not detect short-term fluctuations in corrosion rate which may be related to process upsets. Only an integrated measurement of corrosion rate is obtained.

Materials Comparison

Four materials of construction were investigated in the field study. There was considerable variation in the liquor corrosivity at each mill which concealed the variation between the materials. Coupons of all materials in a given test had similar corrosion rates and the mean rates varied from mill to mill. To separate the two factors, the corrosion rate of individual coupons was plotted vs. the liquor corrosivity. The liquor corrosivity was defined as the average corrosion rate of all coupons exposed during a specified period at a mill. There were

two exposure periods at mill 3. By this means, it could be determined which materials were repeatedly above average in corrosion rate and which were below. A line through the data points was determined by the least squares method and the slope of the line was taken as a measure of the relative corrosion rate. Slopes (m) less than unity indicated a material with corrosion rate below average, and slopes greater than unity indicated above average corrosion rates. The 1018 showed corrosion rates above average (m = 1.24) and A285C was slightly above average (m = 1.15). Lower corrosion rates were observed for A283 (m = 0.92) and A285-SPECIAL (m = 0.78). The results for A285-SPECIAL are illustrated in Figure 8 as an example. Results calculated using the LPR data were ranked similarly (1018: m = 1.24, A285C: m = 1.01, A283: m = 0.99, A285-SPECIAL: m = 0.76). These results confirm that A285 SPECIAL is the best steel (of those tested) for use in white liquor and its corrosion rate is two-thirds that of 1018 ateel. This behavior is probably related to its low Si content and high Cu content.[10] The results also confirm that the effect of steel composition is small compared to the effect of liquor corrosivity on determining corrosion rates.

Liquor Corrosivity

The range of corrosivity of liquors in the test mills is difficult to rationalize. Undoubtedly, much of this difference arises from differences in liquor composition (Table 4). Weight loss studies in this laboratory[12] have shown that small concentrations of $Na_2S_2O_3$ can increase corrosion rates significantly over the long term. Large transients may accompany the addition of $Na_2S_2O_3$ as seen in Figure 2. Results have also shown that S additions (to form polysulfides) can increase corrosion rate. Mill 3 had the highest thiosulfate concentration and also the highest corrosion rates. Some of this thiosulfate may result from oxidation of sulfides through increased contact with air. Mill 4, with the weakest liquor, the lowest thiosulfate (according to sample 1) and a low flow rate had very low corrosion rates. Higher NaOH and Na_2S concentrations observed in the last week are thought to have had little effect on the average corrosion rate; the specimens had reached passive potentials by then.

Flow rates may also have a significant effect on corrosion rates. Studies in this laboratory have shown corrosion rates to increase dramatically in flowing white liquor. Mill 1 had considerable liquor motion and experienced high corrosion rates. The test of flow rate effect in mill 4 was inconclusive because the flow in the clarifier was minimal and so there was very little difference between protected and exposed specimens.

CONCLUSIONS

The linear polarization resistance technique has been shown to be an acceptable method for measuring corrosion rates in kraft white liquors when appropriate corrections are applied, consistent with the measured Tafel slopes. The chief advantage of the linear polarization resistance method is that it can be used to obtain instantaneous measurements of corrosion rate. The electrical resistance technique measured corrosion rates that agreed very well with weight loss measurements and needed no correction or interpretation. It did not give instantaneous measurements which could be correlated with changes in operation. Each method has advantages and disadvantages which might make it more suitable for a particular application.

Materials of construction were ranked in order of decreasing corrosion rates: 1018, A285C, A283 and A285-SPECIAL, confirming that Cu and Ni are beneficial constituents in steel, but Si is detrimental. The liquor corrosivity had a much greater effect on corrosion rate than the material composition.

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TABLE 1 - Composition of Steels Tested

STEEL	C	Mn	P	S	Si	Ni	Cr	Cu	Fe
1018	0.16	0.69	0.018	0.031	0.26	0.03	0.10	0.15	bal
A285C	0.20	0.43	0.010	0.021	--	--	--	--	bal
A283	0.16	0.49	0.012	0.023	0.02	0.01	0.01	0.01	bal
A285SPEC	0.18	0.65	0.019	0.020	0.02	0.01	0.01	0.27	bal

TABLE 2 - Comparison of Weight Loss and LPR Corrosion Rate Measurements of 1018 Steel in Simulated White Liquor

NaOH, g/L	Na_2S, g/L	$Na_2S_2O_3$, g/L	S, g/L	Total Exposure Time, h	Weight Loss Corrosion Rate mpy	Ave. LPR Corrosion Rate mpy	$(\frac{\beta}{Z})^*$ mV
60	20	--	--	508	4.2	11.5	15.8
60	33	--	--	508	4.4	12.4	14.6
60	40	--	--	508	4.0	12.1	13.6
80	33	--	--	508	5.9	15.7	16.1
100	15	--	--	520	4.0	12.9	15.0
100	20	--	--	520	4.4	12.6	15.9
100	25	--	--	520	4.9	14.1	15.0
100	30	--	--	520	4.8	15.9	13.4
100	33	--	--	508	5.3	16.1	14.3
100	33	--	--	568	7.0	20.5	14.2
100	35	--	--	520	4.2	15.0	11.7
100	40	--	--	520	4.4	14.9	12.9
100	45	--	--	520	4.4	13.0	14.6
100	50	--	--	520	4.4	14.0	13.5
120	33	--	--	508	5.4	17.5	13.6
140	33	--	--	508	5.0	16.6	13.2
140	40	--	--	508	5.0	17.6	12.6
100	33	2.5	--	568	20.0	45.5	18.3
100	33	5.0	--	568	18.0	43.0	17.4
100	33	25.0	--	568	28.0	70.5	16.5
100	33	--	0.5	568	10.0	20.5	20.3
100	33	--	2.5	568	17.0	29.5	24.0
100	33	--	5.0	568	5.0	21.5	9.7
100	33	--	10.0	568	2.5	36.0	2.9

TABLE 3 - Anodic and Cathodic Tafel Slopes in Simulated White Liquors

NaOH, g/L	Na_2S, g/L	β_a, mV	β_c, mV	β, mV	$(\frac{\beta}{2})$ mV
60	15	53	98	34.4	17.2
60	20	56	94	35.1	17.6
60	25	58	101	36.8	18.4
60	30	53	98	34.4	17.2
60	35	56	101	36.0	18.0
60	40	53	17	36.5	18.3
80	25	48	109	36.0	18.0
80	40	64	109	40.3	20.1
100	15	56	105	36.5	18.3
100	20	56	110	37.1	18.6
100	25	50	150	37.5	18.8
100	30	46	130	34.0	17.0
100	35	28	84	21.0	10.5
120	10	34	98	25.0	12.5
120	25	48	35	39.0	19.5
140	10	34	34	27.0	13.5
140	15	68	105	41.0	20.5
140	20	31	44	25.5	12.8

TABLE 4 - Mill White Liquor Composition

Mill	Sample No.	NaOH	Na_2S	Na_2CO_3	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	NaCl	Al	Mg	Fe	Cu	Si	Mn	Ca	Na
1	1	92.0	39.2	32.5	4.9	7.1	4.0	14.8	--	--	--	--	--	--	--	--
1	2*	93.9	38.8	32.0	5.4	3.8	3.3	8.5	--	--	--	--	--	--	--	--
1	3*	92.9	39.6	32.5	5.3	4.4	5.1	14.8	--	--	--	--	--	--	--	--
1	4*	98.7	35.7	30.0	2.9	2.9	3.2	6.2	--	--	--	--	--	--	--	--
1	5*	93.4	37.8	27.2	4.5	4.9	4.3	7.3	--	--	--	--	--	--	--	--
1	6*	--	--	--	5.0	6.2	4.4	13.0	--	--	--	--	--	--	--	--
2	1	92.3	41.4	26.9	3.5	3.8	5.4	1.5	--	--	--	--	--	--	--	--
3	1	92.9	31.5	45.1	8.0	3.4	3.8	2.2	--	--	--	--	--	--	--	--
3	2	91.9	44.5	41.8	7.2	7.4	7.8	--	0.18	0.005	0.071	0.004	0.62	--	--	100
3	3	97.3	46.8	40.6	6.7	6.6	4.1	--	0.20	0.005	0.042	0.008	0.44	--	--	100
3	4	110.3	39.8	24.6	4.3	3.2	5.3	1.2	--	--	--	--	--	--	--	--
4	1	87.1	21.7	24.9	2.4	2.3	5.2	1.2	0.01	0.01	0.024	0.002	0.24	0.006	0.34	81
4	2	126.2	30.8	14.0	3.3	4.1	2.8	1.0	--	--	--	--	--	--	--	--
4	3	124.3	36.0	15.3	6.3	6.4	4.3	2.3	--	--	--	--	--	--	--	--

*Samples obtained during periods of high corrosion rate.

TABLE 5 - Comparison of Weight Loss and LPR Corrosion Rate Measurements in Mill White Liquor

Material	Mill	Total Exposure Time, h	Weight Loss, mpy	Anodic LPR, mpy	Cathodic LPR, mpy	Average LPR, mpy	$(\beta/Z)^*$ mV
1018	1	780	29.7	84.8	69.7	77.3	16.0
	1	780	34.9	105.6	80.6	93.1	15.6
	2	400	15.6	--	--	--	--
	2	400	25.0	54.3	23.0	38.6	27.0
	3	858	44.2	61.9	35.0	48.5	38.0
	3	858	41.2	58.5	38.1	48.4	35.5
	3*	912	29.4	--	--	--	--
	3*	912	25.7	--	--	--	--
	4	840	5.8	9.0	9.8	9.4	25.7
	4	840	9.2	11.5	10.1	10.8	35.5
A285C	1	780	23.2	69.4	53.5	61.5	15.7
	1	780	27.1	75.9	53.5	64.7	17.4
	2	400	16.5	--	--	--	--
	2	400	19.5	16.2	23.2	19.7	41.2
	3	858	44.0	57.1	37.8	47.5	38.6
	3	858	41.1	65.2	38.4	51.8	33.0
	3*	912	30.4	--	--	--	--
	4	840	6.4	14.3	13.2	13.8	19.3
	4	840	5.8	11.5	10.9	11.2	21.6
283	1	780	25.8	71.4	54.9	63.2	17.0
	1	780	29.0	78.4	60.8	69.6	17.4
	1	780	25.2	--	--	--	--0
	2	400	18.5	26.0	28.3	27.2	28.3
	2	400	18.8	35.6	26.3	31.0	25.2
	2	400	16.7	--	--	--	--
	3	858	29.3	51.8	28.6	40.2	30.4
	3	858	26.5	47.9	38.0	38.0	29.0
	3	858	23.7	--	--	--	--
	3*	912	18.1	--	--	--	--
	4	840	7.5	10.9	10.1	10.5	29.7
	4	840	7.1	10.9	10.6	10.8	27.4
	4	840	7.3	--	--	--	--
A285SPEC	1	780	22.9	34.7	34.4	34.6	27.6
	1	780	23.9	58.5	42.3	50.4	19.7
	1	780	21.1	--	--	--	--
	2	400	14.2	24.1	23.2	23.7	25.0
	2	400	14.2	23.2	21.6	22.4	26.4
	2	400	11.4	--	--	--	--
	3	858	27.8	45.9	28.0	37.0	31.3
	3	858	27.1	50.1	30.0	40.0	28.2
	3	858	21.4	--	--	--	--
	3*	912	8.9	--	--	--	--
	4	840	6.2	10.4	11.2	10.8	23.9
	4	840	6.1	10.9	10.9	10.9	23.3
	4	840	7.6	--	--	--	--

*These results were obtained during a separate exposure.

TABLE 6 - Tafel Slopes Measured from Polarization Curves

Material	Mill	β_a	β_c
1018	1	--	150
	2	60	120
	4	--	110
A285C	1	60	140
	2	65	120
	4	--	130
A283	1	60	130
	2	60	110
	4	70	140
A285SPEC	1	110	115
	2	60	130
	4	85	110

TABLE 7 - Comparison of Corrosion Rates Measured by Weight Loss and ER Methods

Environment	ER, mpy	Weight Loss, mpy
100 g/L NaOH + 33 g/L Na_2S	13	13
100 g/L NaOH + 33 g/L Na_2S + 5 g/L S	1	3
100 g/L NaOH + 33 g/L Na_2S + 10 g/L S	3	5
100 g/L NaOH + 33 g/L Na_2S + 5 g/L $Na_2S_2O_3$	20	23
100 g/L NaOH + 33 g/L Na_2S + 5 g/L $Na_2S_2O_3$	23	12
100 g/L NaOH + 33 g/L Na_2S 25 g/L $Na_2S_2O_3$	44	42
Mill 3	25	29.4, 25.7, 30.9
Mill 3	32	41.2, 44.2
Mill 4	6	5.8, 9.2

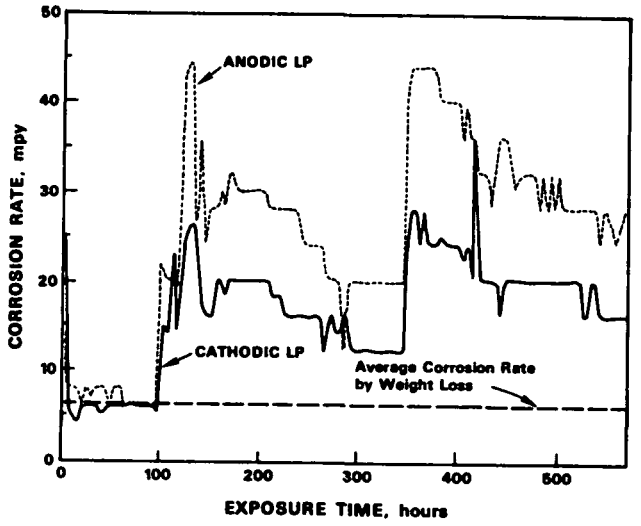

Figure 1 - Corrosion rate measured directly from the linear polarization resistance instrument (β/z = 41.65 mV) during laboratory exposure. Average weight loss corrosion rate is plotted for comparison.

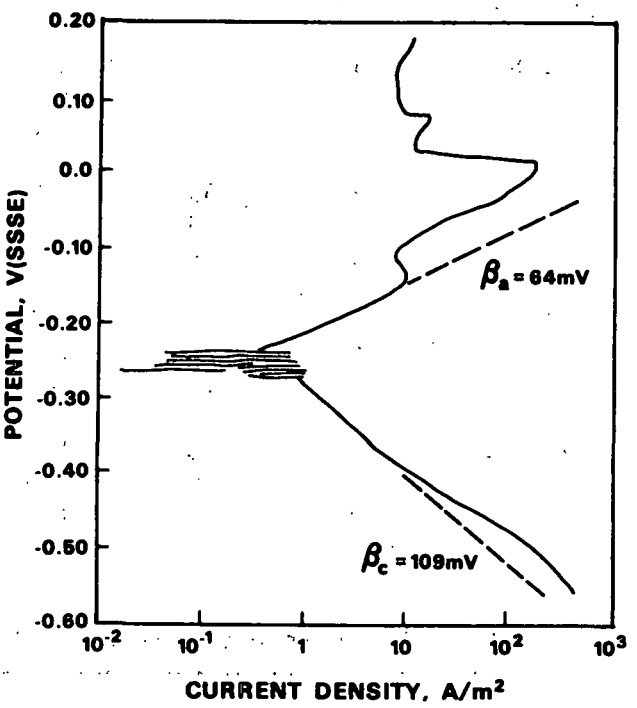

Figure 3 - Polarization curve for 1018 steel in NaOH + Na_2S solution, 90 C, 1 mV/s.

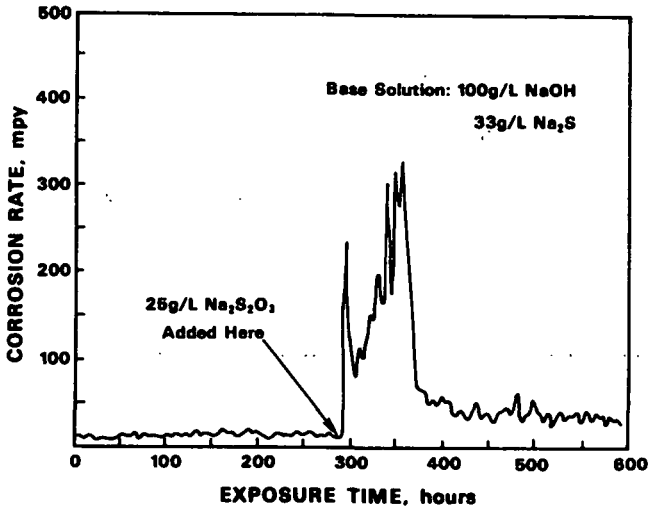

Figure 2 - Increase of corrosion rate following $Na_2S_2O_3$ addition as measured directly from the linear polarization resistance instrument.

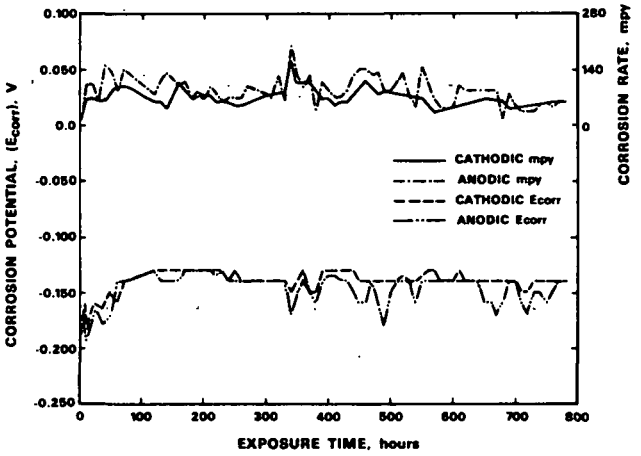

Figure 4 - Representative linear polarization resistance results. 1018 steel in mill 1.

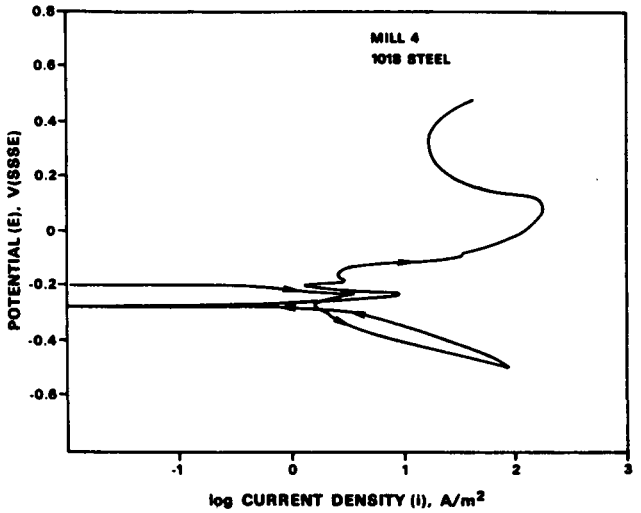

Figure 5 - Typical in-mill polarization curve obtained in mill 4, 0.6 V/h.

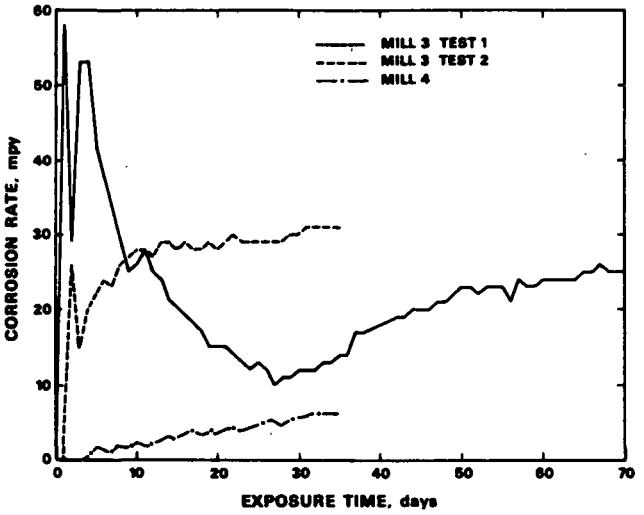

Figure 7 - Corrosion rate measured by electrical resistance technique in mill white liquor.

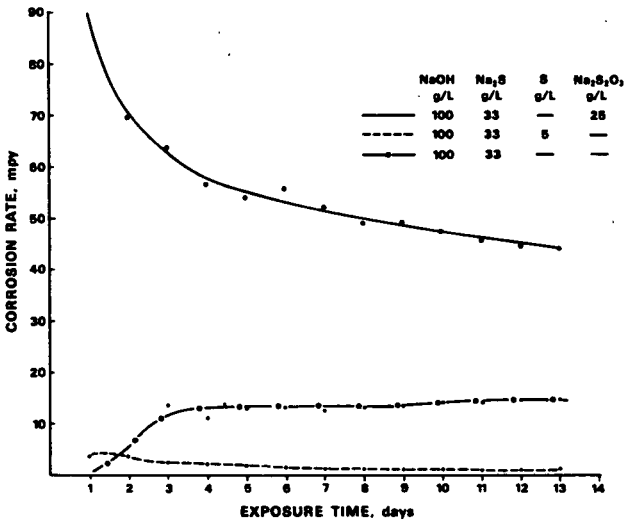

Figure 6 - Corrosion rate measured by electrical resistance technique in simulated white liquors.

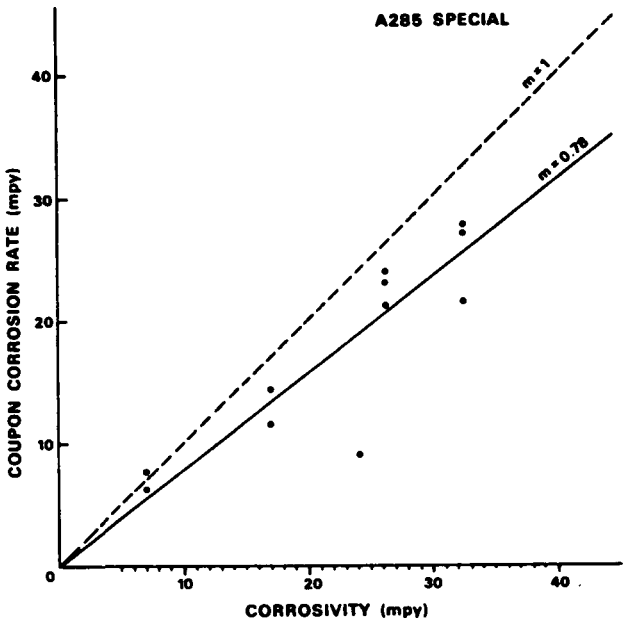

Figure 8 - Corrosion rate of A285-SPECIAL coupons vs. mill liquor corrosivity. The line with slope m = 1 represents the average corrosion rate for all materials in a mill test.